

II.1.6 Robust Low-Cost Water-Gas Shift Membrane Reactor for High-Purity Hydrogen Production from Coal-Derived Syngas

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- Develop and demonstrate a selected Pd/Cu coated Ta membrane with improved durability.
- Construct and demonstrate a bench-scale WGS membrane reactor.
- Demonstrate the scalability of the technology by constructing a 500 L hydrogen/hr production capacity unit.
- Perform a study on the economic feasibility of the WGS membrane reactor.
- Analyze cost benefits of the demonstrated WGS membrane reactor technology.



Introduction

There exists a need to develop a lower cost, robust WGS membrane reactor that can be used to process coal-derived syngas for the production of high-purity hydrogen. The required characteristics of this WGS membrane reactor are a contaminant-tolerant, highly active WGS catalyst and a selective Pd/Cu coated Ta membrane with improved durability. Such a membrane reactor should be constructed and demonstrated at the bench-scale to demonstrate the scalability of the technology, preferably at 500 L hydrogen/hr production capacity. WGS membrane reactors incorporating a highly selective H_2 -permeable membrane offer the advantages of: 1) generating more hydrogen in a single reactor, instead of conventional two-stage (high-temperature and low-temperature) shift process, 2) simplifying or completely eliminating downstream hydrogen separation and purification processes, and 3) producing a high-pressure stream of predominantly CO_2 for cost-effective capture and sequestration. However, despite these obvious advantages, H_2 generation from syngas employing WGS membrane reactors has not been commercialized in any significant scale, primarily due to the unavailability of reliable, high-performance and economical membrane reactors and WGS catalysts. This project will address these technical barrier issues.

Approach

Initial work will be directed towards the development of a contaminant-tolerant, highly active WGS catalyst (MoS_2 -based with added modifiers). A suitable Pd/Cu coated Ta membrane, capable of promoting H_2 dissociation/association reactions in the presence of S and Cl, with improved durability, will

Objectives

- Develop a water-gas shift (WGS) membrane (Figure 1) that replaces multiple process units with a single catalytic membrane reactor, has high process efficiency realized by improving hydrogen yield at low steam to carbon ratios, and produces a high-pressure CO_2 -rich stream potentially suitable for sequestration.
- Develop a lower cost, robust WGS membrane reactor that can be used to process coal-derived syngas for the production of high-purity hydrogen.
- Develop and demonstrate a contaminant-tolerant, highly active WGS catalyst.

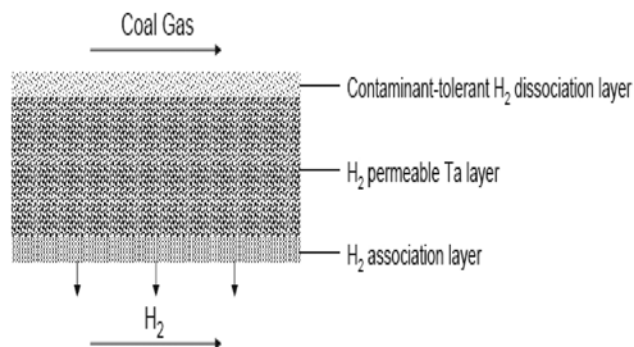


FIGURE 1. Membrane Design

then be selected for development and demonstration. Both the WGS catalyst and the H₂-selective membrane must be capable of operating at 300-500°C, 300-500 psig and remain tolerant of high concentrations of H₂S and HCl. Using data from these tests, a bench-scale WGS membrane reactor will then be constructed and demonstrated. Finally, to show that the WGS membrane reactor technology is scalable, a 500 L hydrogen/hr system will be built and an economic feasibility study of the WGS membrane reactor will then be performed.

Accomplishments

- Completed preparation of 10-16 samples of both alumina-supported and unsupported nano-sized Mo₂C and sulfided Mo, MoCo and CoCr catalysts and completed characterization of the catalysts by investigating the structural properties and determining their surface area, pore size, agglomerate size, composition, and crystallinity.
- Completed evaluation of the catalysts prepared in Q1 and compared with commercial high-temperature WGS catalysts for their WGS activity and stability in a high-pressure fixed-bed catalyst testing system. Identified and selected the most active and stable WGS catalysts and the best operating conditions.
- Completed the development of Pd/Cu-coated Ta tubular H₂ membrane elements and studied the use of an electroless plating method to fabricate Pd/Cu-coated Ta membrane tubes with different wall thicknesses.
- Identified contaminant-tolerant WGS catalysts with high activity over a wide temperature range (300-500°C). The catalysts demonstrated excellent durability in the presence of 3,000 ppm H₂S and 350 ppm HCl for over 220 hours (see Table 1).

TABLE 1. Result Summary – WGS Catalyst

Performance Criteria	Current Status	Targets		This Work
		2010	2015	
Catalyst Form	Pellets	Advanced configurations – TBD		Pellets
Active Metal	Cu/Zn or Fe/Cr or Co/Mo	Advanced configurations – TBD		Mo
Feed Temperature (°C)	200-300	>250	>400	>250
Feed Pressure (psia)	450-1150	>450	>750	415
Approach to Equilibrium (°C)	8-10	<6	<4	<4
Min. H ₂ O/CO Ratio	2.6	<2.6	<2	<2
Sulfur Tolerance (ppm _w)	varies	>20	>100	3000
COS Conversion	varies	Partial	Total	-
Chloride Tolerance (ppm _w)	varies	>3	>100	350
Durability (y)	3-7	>7	>10	-
Catalyst Cost (\$/lb)	~5	<5	<5	-

- Identified dense metal membranes with high H₂ permeability and selectivity. The membranes maintained high permeability in the presence of 2,000 ppm H₂S and 33% H₂O.

Future Directions

- Complete characterization and testing for H₂ separation (see Table 2) in order to identify and select the most stable and efficient membranes and associated membrane preparation parameters for building a WGS reactor and scale-up.

TABLE 2. Result Summary – Hydrogen Separation

Performance Criteria	Current Status			Targets			This Work
	Microporous	Cermet	Dense Ceramic	2007	2010	2015	
Flux (scfh/ft ²)	20-100	~300	2	100	200	300	20
Temperature (°C)	300-600	300-400	900	400-700	300-600	250-500	350-550
S Tolerance (ppm _w)	Yes	~20	-	-	20	>100	2000
Cost (\$/ft ²)	150-200	<200	-	150	100	<100	-
WGS Activity	No	-	-	Yes	Yes	Yes	Yes
ΔP Capability (psig)	100	1000	-	100	400	800	400
CO Tolerance	Yes	Yes	-	Yes	Yes	Yes	-
H ₂ Purity (%)	90-98	>99.999	-	95	99.5	99.99	>99.9
Durability (y)	-	0.9	-	1	3	5	-

- Quantify performance and stability of membrane in contaminant-laden syngas.
- Examine membrane microstructure in order to relate permeability to structure and synthetic parameters.
- Fabricate and demonstrate integrated WGS membrane reactor.
- Conduct cost analysis.